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Elastic scattering of very slow electrons by molecules

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The modified effective-range theory, which has enjoyed great success in its application to electron-atom scattering, is hereby extended to electron scattering from molecules. An analytic expression for the diffusion cross section for molecules in any rotational state is obtained. It is utilized to analyze the detailed results of recent swarm experiments on H_2, and to comment on the less-detailed experimental results on D_2, N_2, and O_2.

I. INTRODUCTION

Much elegant theoretical work on low-energy electron scattering from atoms has been accomplished by Spruch and co-workers[1] by taking advantage of the analytic long-range potentials. In particular, they have obtained expressions for the partial-wave phase shifts as power series of the magnitude of the wave vector k (and $\ln k$) for the induced polarization potentials, the dipole $-\alpha r^{-4}$, and the quadrupole $-\gamma r^{-6}$ (where α is the dipole and γ the quadrupole polarizabilities).[2] The results known as modified effective-range theory (MERT) have been confirmed by experiments on the rare gases.[3(a)] Best results are obtained by comparison of the diffusion or momentum-transfer cross sections,[3(b)] where experimental values are available for energies as low as the meV range.

The primary purpose of this paper is to show that MERT can readily be extended to electron-molecule scattering. In the present work we will restrict the molecules to homonuclear diatomics in the ${}^1\Sigma_g$ state. Thus we exclude the extremely-long-range dipole potential, and avoid very complicated coupling coefficients in a more general case. Thus in addition to the potentials present in the atom case, we now encounter a quadrupole potential given by $-eQr^{-3}P_2(\cos\theta)$, where Q is the molecule's quadrupole moment in units of ea_0^2 and θ is the angle between the electron and the molecular axis. It should be noted that this potential is also present in electron-atom scattering if the atom is not in an S state. In fact, the present work applies to that case as well, and one only needs to replace the molecular rotational state j by the atomic fine-structure state.

Actually, the effective-range theory for a potential of the form r^{-3} has been derived by Shakeshaft.[4] He concluded that the s-wave phase shift was infinite, and hence the scattering length did not exist, and that for all non-s-waves the phase shifts were all linear in k. Fortunately, the situation of interest here is not the isotropic r^{-3} potential but the quadrupole potential, which contains a factor P_2. This factor eliminates the pure s-wave contribution through group-theoretical considerations, and therefore the MERT s-wave phase shift for molecules is the same as for atoms. However, for non-s waves, this factor introduces a coupling coefficient which does not vanish. Therefore, the non-s-wave phase shifts are now linear in k rather than quadratic, as in the atom case. This fact might lead one to expect the diffusion cross section for molecules to be substantially different from the case for atoms.

Experimentally, many data on diffusion cross sections are available.[5] We shall focus our attention on the recent data of Crompton and co-workers,[6,7] which are believed to be accurate to 5%. These are obtained from swarm experiments conducted at 77°K, including three cases of particular interest: (i) parahydrogen H_2 (99.5% in the $j=0$ state); (ii) normal hydrogen H_2 (24.9% in the $j=0$ state and 75.0% in the $j=1$ state); and (iii) normal deuterium D_2. These results should agree well with the predictions of MERT when properly modified, as in this work at sufficiently low energies—say, less than 0.1 eV, safely below the vibrational-excitation threshold. At these low energies, only elastic and rotational excitation and deexcitation processes are energetically possible.

The reader is reminded that in the swarm experiment cross sections are inferred from measurements of transport properties of the gas (particularly the electron drift velocity and the ratio of diffusion coefficient to mobility), fitted to solutions of the Boltzmann equation. Details of this procedure are given by Crompton *et al.*[6] and elsewhere,[5(b)] and will not be repeated here. We only wish to emphasize that cross sections so obtained are absolute, and that errors in one cross section will affect the accuracy of the other cross sections. Clearly, the fewer cross sections there are (i.e., energetically allowed), the more reliable they are. In fact, in experiment i on parahydrogen, there are essentially only two possible processes: elastic scattering ($j=0\rightarrow 0$) and rotational excitation ($j=0\rightarrow 2$). Other allowed processes are generally negligible either because of a very small cross section, e.g., ($j=0\rightarrow 4$), or because of the small population of the initial state, e.g., 0.5% for $j=2$. Under these simple conditions, cross sections for these two processes can be determined uniquely and accurately from the swarm data. The excitation cross section has already been studied theoretically,[8] and is found to be in good agreement with experiment. In Sec. II we will show that the MERT diffusion cross section for $j=0$ is identical to the expression for atoms, and comparison will be made between theory and experiment.

In experiment ii on normal hydrogen, there are now four cross sections to consider: the diffusion cross sections for $j=0$ and for $j=1$ and the excitation cross sections ($j=0\rightarrow 2$) and ($j=1\rightarrow 3$). As pointed out by Crompton *et al.*,[6] these cross sections are now no longer uniquely determined. To facilitate their analysis, they have assumed that the two diffusion cross sections are equal, based on the results of a close-coupling calculation.[9] By obtaining the MERT diffusion cross section for any rotational state $\sigma_d(j)$, we will be able to investigate the validity of their assumption and hence the reliability of the entire procedure used to determine the other cross sections.

In Sec. IV we will discuss the experiment-iii results on D_2 in light of the new theory. Analysis will also be made on other homonuclear diatomic gases for which swarm data are available.[5(b)] In particular, we will consider nitrogen and oxygen. Finally, in Sec. V we present the conclusion.

II. GENERAL FORMULATION AND RESULTS FOR PARAHYDROGEN

Recently the general theory of electron-molecule scattering has been explicated in two alternative frames of coordinates, the molecular frame and the laboratory frame.[10] In the energy range of interest, $E \lesssim 0.1$ eV and hence $k \lesssim 0.08 a_0^{-1}$, corresponding to a wavelength of $\gtrsim 12 a_0$. This implies that the electron-molecule interaction takes place primarily at large distances and that therefore the laboratory frame is the appropriate frame to use. Furthermore, we need not know the complicated short-range potentials, because they are not probed by electrons with long wavelengths. Our task then is to evaluate laboratory-frame phase shifts from the long-range potentials in a.u. ($m=e=\hbar=a_0=1$), given by

$$V(\vec{r}) = -\frac{1}{2}\frac{\alpha_0}{r^4} - \frac{1}{2}\frac{\alpha_2}{r^4}P_2(\cos\theta) - \frac{Q}{r^3}P_2(\cos\theta). \quad (1)$$

The first term is the familiar induced-polarization potential, except that the polarizability tensor is expressed as an isotropic part α_0 and an anisotropic part α_2, which appears in the second term. The third term is the quadrupole potential. Other potentials may be neglected, since our primary interest is to determine the momentum cross section at very low energies. To be precise, we will evaluate only the two leading terms for $\sigma_d(j)$, i.e., the constant and the linear term in k. It can be shown that potentials which fall off as r^{-5} or faster and short-range potentials can only contribute to the higher-order terms neglected here.[2]

The diffusion cross section is related to the differential cross section by

$$\sigma_d = \int \frac{d\sigma}{d\Omega}(1-\cos\theta)\,d\Omega. \quad (2)$$

A more explicit form in terms of laboratory-frame T matrices has been obtained by Arthurs and Dalgarno,[11]

$$\begin{aligned}\sigma_d(j) = \frac{\pi}{(2j+1)k^2}\Bigg(&\sum_{Jll'}(2J+1)\,T^{Jj*}_{l'l}\,T^{Jj}_{l'l} + \frac{1}{3}\sum_{J_1 J_2 l_1 l_1' l_2 l_2'}(-1)^{1/2(-l_1+l_2-l_1'+l_2')}\\ &\times\left[(2l_1+1)(2l_1'+1)(2l_2+1)(2l_2'+1)\right]^{1/2}(2J_1+1)(2J_2+1)\,T^{J_1 j*}_{l_1' l_1}\,T^{J_2 j}_{l_2' l_2}\\ &\times(l_1 0 l_2 0|10)(l_1' 0 l_2' 0|10)\begin{Bmatrix} l_2 & l_1 & 1\\ J_1 & J_2 & j\end{Bmatrix}\begin{Bmatrix} l_2' & l_1' & 1\\ J_1 & J_2 & j\end{Bmatrix}\Bigg). \quad (3)\end{aligned}$$

The index l represents the orbital angular momentum of the electron and J the invariant total angular momentum of the electron-molecule system. The $(\ldots.|\ldots)$ are Clebsch-Gordan coefficients; $\{: : :\}$ are $6j$ symbols.

Clearly, conservation of angular momentum requires $\vec{J}=\vec{l}+\vec{j}$, which is reflected in the 6-j symbols. In Eq. (3) the T matrices are not necessarily diagonal in l, since the scattering potential V contains terms that are not isotropic. However, the nondiagonal T matrices are expected to be small, since l is an approximate good quantum number. This phenomenon, known as l uncoupling, is what makes the laboratory frame appropriate. Note that for the special case of $j = 0$ these nondiagonal T matrices are identically zero, due to angular-momentum considerations. The diagonal T matrices are related to phase shifts η^J_{jl} in the usual manner,

$$T^{Jj}_{ll} = 2ie^{i\eta^J_{jl}} \sin\eta^J_{jl} . \tag{4}$$

Now if we neglect terms involving nondiagonal T matrices, Eq. (3) simplifies considerably:

$$\sigma_d(j) = \frac{4\pi}{(2j+1)k^2} \left(\sum_{J,l} (2J+1)\sin^2\eta^J_{jl} + \frac{1}{3} \sum_{J_1,J_2,l_1 l_2} (-1)^{-l_1+l_2}(2l_1+1)(2l_2+1)(2J_1+1)(2J_2+1) \right.$$
$$\left. \times \sin\eta^{J_1}_{jl_1} \sin\eta^{J_2}_{jl_2} \cos(\eta^{J_1}_{jl_1} - \eta^{J_2}_{jl_2})(l_1 0 l_2 0|10)^2 \begin{Bmatrix} l_2 & l_1 & 1 \\ J_1 & J_2 & j \end{Bmatrix}^2 \right). \tag{5}$$

Since l_1 and l_2 can only differ by 1, Eq. (5) can be further simplified. After some manipulation, we obtain

$$\sigma_d(j) = \frac{4\pi}{(2j+1)k^2} \sum_{l,J_1,J_2} (l+1)(2J_1+1)(2J_2+1) \times \begin{Bmatrix} J_2 & J_1 & 1 \\ l & l+1 & j \end{Bmatrix}^2 \sin^2(\eta^{J_1}_{jl} - \eta^{J_2}_{jl+1}). \tag{6}$$

This form now resembles the expression for the diffusion cross sections in atoms. In fact, for the ground rotational state ($j = 0$), σ_d reduces to the familiar expression

$$\sigma_d(0) = \frac{4\pi}{k^2} \sum_l (l+1)\sin^2(\eta^l_{0l} - \eta^{l+1}_{0l+1}). \tag{7}$$

Indeed, the anisotropic parts of V do not contribute to this case at all, since in the $j = 0$ state the molecule appears to the electron as an isotropic charge distribution. Therefore the MERT results without any modification can be applied to the results[6] of experiment i. For the sake of completeness and for future reference, we reproduce the MERT results here[1]:

$$\tan\eta_0 = -Ak - \tfrac{1}{3}\pi\alpha_0 k^2 - \tfrac{4}{3}\alpha_0 A k^3 \ln[\tfrac{1}{4}(\alpha_0)^{1/2}k] + O(k^3) \tag{8}$$

and

$$\tan\eta_l = \frac{\pi\alpha_0 k^2}{(2l-1)(2l+1)(2l+3)} + O(k^3), \quad \text{for } l \geq 1. \tag{9}$$

Here A is the scattering length, which is a parameter containing all our ignorance of the short-range potentials. Note that in Eq. (7) the superscript is redundant, since $J = l$. Substituting Eqs. (8) and (9) into (7), we obtain the familiar expression

$$\sigma_d(0) = 4\pi A^2[1 + (4\pi/5A)\,\alpha_0 k + \cdots] . \tag{10}$$

Note that only s and p waves contribute to this expression through the term $l = 0$ in Eq. (7). Higher partial waves affect only terms of order k^2 or higher, and therefore do not appear in Eq. (10).

In Fig. 1 we show the experimental diffusion cross section plotted versus the wave vector k. It is observed that a straight line fits the data very well (except at the point $k = 0$).[12] From the

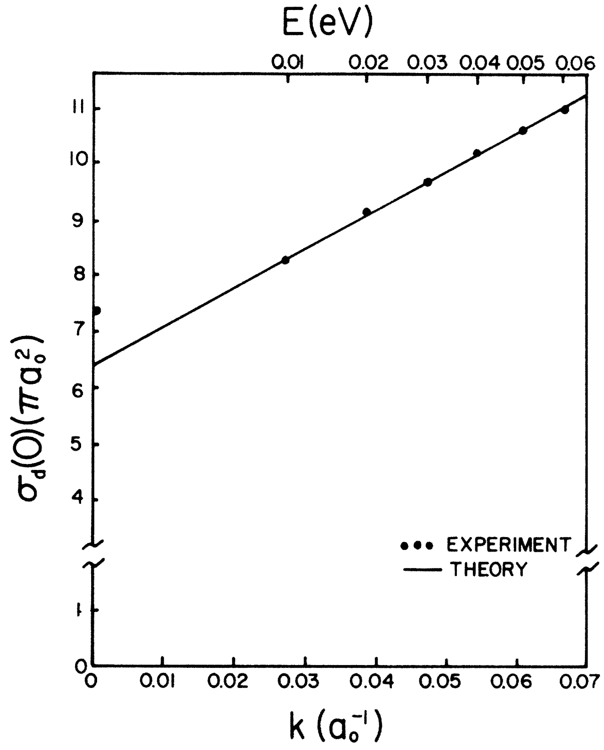

FIG. 1. Diffusion cross section in parahydrogen at 77 °K, as a function of the wave vector k (bottom scale) and as a function of the energy E (top scale).

intercept, we determine that $A = 1.26a_0$, while from the slope we obtain $\alpha_0 = 5.5a_0^3$. This value of the polarizability is in good agreement with the elaborately calculated value[13] of $5.41a_0^3$ and an independent experimental value[14] of $5.44a_0^3$.

It is worthwhile to comment on the point at $k = 0$. According to the principle of detail balance, the superelastic cross section $\sigma(j = 2 \rightarrow 0)$ can be obtained from the known excitation cross section[6,8] $\sigma(j = 0 \rightarrow 2)$. Thus we have

$$\sigma(j = 2 \rightarrow 0) = \left(\frac{k^2 + 6B}{k^2}\right)^{1/2} \left(\frac{1}{5}\right) \frac{16}{45} Q^2(\pi a_0^2), \qquad (11)$$

where B is the rotational constant $= 2.8 \times 10^{-4}$ a.u. and $Q = 0.48$ for H_2. Ordinarily, we may ignore this cross section, as it is small in comparison with the elastic cross section, and furthermore it is weighted by the initial population of 0.5%. However, at $k = 0$, it is seen from Eq. (11) that this cross section becomes infinite, which complicates the analysis of the swarm data. Furthermore, as there are so few electrons with energy approaching zero in a thermal swarm at 77°K, σ_d at zero energy cannot be reliably determined.

Perhaps it should be emphasized that, in the energy range of Fig. 1 corresponding to $k \approx 0.03$–$0.07a_0^{-1}$, the first correction term in the bracket of Eq. (10), $\frac{8}{3}\alpha_0 k^2 \ln(\frac{1}{4}\alpha_0^{1/2}k)$, is not entirely negligible. Typically $\ln(\frac{1}{4}\alpha_0^{1/2}k) \approx -3$ and the correction term ($\approx -44k^2$) may introduce an error of around 10% in the cross section. More significantly, this correction term does account for the down-turning of the experimental points at the higher-energy side of Fig. 1.

III. RESULTS IN GENERAL CASE AND NORMAL HYDROGEN

Next we turn our attention to experiment ii, where the molecule is not necessarily in the ground rotational state. It is therefore desirable to evaluate the general diffusion cross section $\sigma_d(j)$ given by Eq. (3). However, following our earlier arguments, we expect the dominant contribution to come from diagonal T matrices. Therefore it is convenient to break up Eq. (3) into terms containing only diagonal T matrices, as given by Eq. (6), and terms involving nondiagonal T matrices. We will first evaluate these diagonal terms, then the nondiagonal T-matrix contributions, and finally the cross terms between diagonal and nondiagonal T matrices.

A. Diagonal T matrices, $l = 0$

For the diagonal T matrices, we merely need to evaluate the phase shifts in Eq. (6), given the potentials in Eq. (1). According to the two-potential formula,[2] to the accuracy in which we are interested the effect of each term in the potential on the phase shifts is additive, and furthermore, the Born results are adequate. Of course, the first term gives the well-known results of Eqs. (8) and (9). The second and the third can be written as the product of a radial function and an angular function P_2. The effect of the factor P_2 on the phase shift η_{jl}^J may be evaluated by Racah algebra[15]:

$$(jl, J|P_2|jl, J) = (-1)^J \tfrac{1}{5}(2j+1)(2l+1) \times (l0l0|20)(j0j0|20) \begin{Bmatrix} j & l & J \\ l & j & 2 \end{Bmatrix}. \qquad (12)$$

Clearly, it vanishes whenever $j = 0$ or $l = 0$. This substantiates our earlier physical argument that for the ground rotational state ($j = 0$) the MERT results for molecules reduce to those for atoms. However, for other rotational states ($j \neq 0$), Eq. (12) will not vanish except for the s wave. Following Shakeshaft[4] the radial integrals can be evaluated analytically,[16]

$$-2k \int_0^\infty j_l^2(kr) \frac{Q}{r^3} r^2\, dr = \frac{Qk}{l(l+1)}, \quad \text{for } l \geq 1. \qquad (13)$$

Thus the net effect of the anisotropic potential is to modify the non-s phase shifts by the following:

$$\tan\eta_{jl}^J = \tan\eta_l + (-1)^J \tfrac{1}{5}(2j+1)(2l+1) \times (l0l0|20)(j0j0|20) \begin{Bmatrix} j & l & J \\ l & j & 2 \end{Bmatrix} \times \left(\frac{Qk}{l(l+1)} + \frac{\pi\alpha_2 k^2}{(2l-1)(2l+1)(2l+3)}\right). \qquad (14)$$

Note that the additional contribution due to the quadrupole moment results in a term that is one power in k *lower* than in the atomic case. This can be expected, since the new potential falls off as r^{-3}, in comparison with the old atomic r^{-4}. Hence all partial waves now contribute to the lowest-order term in $\sigma_d(j)$. Still, the dominance of the centrifugal barrier at low energies dictates that the cross section be determined by the few lowest partial waves. To see this clearly and to facilitate comparison with Eq. (10), we will evaluate the cross section as given by Eq. (6) first for $l = 0$, then for all terms $l \geq 1$, and the summed results.

Accordingly, the term $l = 0$ in Eq. (6) gives

$$\sigma_d(j)_{l=0} = \frac{4\pi}{(2j+1)k^2} \sum_J (2J+1)(2j+1) \times \begin{Bmatrix} J & j & 1 \\ 0 & 1 & j \end{Bmatrix}^2 \sin^2(\eta^j_{j0} - \eta^J_{j1}). \tag{15}$$

We may replace the sine function by its argument since the phase shifts are all small ($\propto k$) and we will neglect terms of order k^3. From Eqs. (9) and (14) we obtain

$$\eta^j_{j0} - \eta^J_{j1} = -Ak - \tfrac{1}{3}\pi\alpha_0 k^2 - \frac{\pi}{15}\alpha_2 k^2 - (-1)^J \tfrac{1}{5}(2j+1)\,3(1010|20)(j0j0|20) \times \begin{Bmatrix} j & 1 & J \\ 1 & j & 2 \end{Bmatrix} \left(\frac{Qk}{2} + \frac{\pi\alpha_2 k^2}{15}\right). \tag{16}$$

Substituting Eq. (16) into Eq. (15) and simplifying, we have

$$\sigma_d(j)_{l=0} = \frac{4\pi}{k^2} \sum_J \frac{(2J+1)}{3(2j+1)} \left[(-Ak - \tfrac{2}{5}\alpha_0\pi k^2) - (-1)^{J+j+1}\,3(2j+1) \times \frac{j(j+1)}{(2j-1)(2j+1)(2j+3)} \begin{Bmatrix} j & 1 & J \\ 1 & j & 2 \end{Bmatrix} \left(\frac{Qk}{2} + \frac{\pi\alpha_2 k^2}{15}\right)\right]^2. \tag{17}$$

It is understood that J runs from $j-1$ to $j+1$, owing to the usual triangular restriction. In multiplying out the squares in Eq. (17), we obtain three terms. The first term is simply the familiar expression, as for atoms given by Eq. (10). The second term contains the factor

$$\sum_J (2J+1) \begin{Bmatrix} j & 1 & J \\ 1 & j & 2 \end{Bmatrix} \begin{Bmatrix} j & 1 & J \\ 1 & j & 0 \end{Bmatrix}, \tag{18}$$

where we have introduced the second 6-j symbol, which is simply $(-1)^{J+j+1}[3(2j+1)]^{-1}$. Owing to the orthonormality property of the 6-j symbols given below,[17]

$$\sum_J (2J+1)(2L+1) \begin{Bmatrix} j & l & J \\ l' & j' & L \end{Bmatrix} \begin{Bmatrix} j & l & J \\ l' & j' & L' \end{Bmatrix} = \delta_{LL'}, \tag{19}$$

the expression given by (18) is zero and the cross term in Eq. (17) is seen to vanish. Finally, the third term in Eq. (17) may be written as

$$4\pi \sum_J (2J+1) \begin{Bmatrix} j & 1 & J \\ 1 & j & 2 \end{Bmatrix}^2 \frac{3(2j+1)j(j+1)}{(2j-1)(2j+1)(2j+3)} \times \left(\frac{Q}{2} + \frac{\pi\alpha_2 k}{15}\right)^2.$$

Applying the sum rule [Eq. (19)] we obtain

$$4\pi \frac{3j(j+1)}{5(2j-1)(2j+3)} \left(\frac{Q^2}{4} + \frac{\pi\alpha_2 Qk}{15}\right). \tag{20}$$

Recalling Eq. (10), we see that the presence of the quadrupole moment introduces a small correction to the bracket equaling

$$\frac{3j(j+1)Q^2}{20(2j-1)(2j+3)A^2} = 0.06\left(\frac{Q}{A}\right)^2, \quad \text{for } j=1.$$

For H_2, $Q/A = 0.48/1.26$, and the correction is about 1% at $k=0$.

B. Diagonal T matrices, $l \geqslant 1$

The remaining terms in Eq. (6) are

$$\begin{aligned}\sigma_d(j) = \frac{4\pi}{(2j+1)k^2} \sum_{l=1} \sum_{J_1 J_2} (l+1)(2J_1+1)(2J_2+1) \begin{Bmatrix} J_2 & J_1 & 1 \\ l & l+1 & j \end{Bmatrix}^2 \\ \times \Bigg[(-1)^{J_1} \tfrac{1}{5}(2j+1)(2l+1)(l0l0|20)(j0j0|20) \begin{Bmatrix} j & l & J_1 \\ l & j & 2 \end{Bmatrix} \left(\frac{Qk}{l(l+1)} + \frac{\pi\alpha_2 k^2}{(2l-1)(2l+1)(2l+3)}\right) \\ - (-1)^{J_2} \tfrac{1}{5}(2j+1)(2l+3)(l+1\,0\,l+1\,0|20)\,(j0j0|20) \begin{Bmatrix} j & l+1 & J_2 \\ l+1 & j & 2 \end{Bmatrix} \frac{Qk}{(l+1)(l+2)} \\ + \frac{\pi\alpha_2 k^2}{(2l+1)(2l+3)(2l+5)} + \frac{\pi\alpha_0 k^2}{(2l-1)(2l+1)(2l+3)} - \frac{\pi\alpha_0 k^2}{(2l+1)(2l+3)(2l+5)} \Bigg]^2.\end{aligned} \tag{21}$$

Combining the last two terms, squaring, and dropping terms of order k^2, we have

$$\begin{aligned}\sigma_d(j)_{l\geq 1}=4\pi\Bigg[&\sum_{l=1}\sum_{J_1J_2}(l+1)(2J_1+1)(2J_2+1)\begin{Bmatrix}J_2 & J_1 & 1\\ l & l+1 & j\end{Bmatrix}^2\tfrac{1}{25}(2j+1)(2l+1)^2(l0l0|20)^2(j0j0|20)^2\\
&\times\begin{Bmatrix}j & l & J_1\\ l & j & 2\end{Bmatrix}^2\left(\frac{Q^2}{l^2(l+1)^2}+\frac{2\pi\alpha_2Qk}{l(l+1)(2l-1)(2l+1)(2l+3)}\right)+\tfrac{1}{25}(2j+1)(2l+3)^2(l+1\,0\,l+1\,0|20)^2\\
&\times(j0j0|20)^2\begin{Bmatrix}j & l+1 & J_2\\ l+1 & j & 2\end{Bmatrix}^2\left(\frac{Q^2}{(l+1)^2(l+2)^2}+\frac{2\pi\alpha_2Qk}{(l+1)(l+2)(2l+1)(2l+3)(2l+5)}\right)\\
&-2(-1)^{J_1+J_2}\tfrac{1}{25}(2j+1)(2l+1)(2l+3)(l0l0|20)(l+1\,0\,l+1\,0|20)(j0j0|20)^2\\
&\times\begin{Bmatrix}j & l & J_1\\ l & j & 2\end{Bmatrix}\begin{Bmatrix}j & l+1 & J_2\\ l+1 & j & 2\end{Bmatrix}\left[\frac{Q^2}{l(l+1)^2(l+2)}+\frac{\pi\alpha_2Qk}{(l+1)(2l+1)(2l+3)}\left(\frac{1}{l(2l+5)}+\frac{1}{(l+1)(2l-1)}\right)\right]\\
&+2(-1)^{J_1}\frac{1}{5}\,\frac{(2l+1)}{l(l+1)}\,(l0l0|20)(j0j0|20)\begin{Bmatrix}j & l & J_1\\ l & j & 2\end{Bmatrix}\frac{12\pi\alpha_0Qk}{(2l-1)(2l+1)(2l+3)(2l+5)}\\
&-2(-1)^{J_2}\frac{1}{5}\,\frac{(2l+3)}{(l+1)(l+2)}\,(l+1\,0\,l+1\,0|20)(j0j0|20)\begin{Bmatrix}j & l+1 & J_2\\ l+1 & j & 2\end{Bmatrix}\\
&\times\frac{12\pi\alpha_0Qk}{(2l-1)(2l+1)(2l+3)(2l+5)}\Bigg]. \qquad (22)\end{aligned}$$

This expression can be greatly simplified by applying Eq. (19) and the following sum rules[17]:

$$\sum_{j_{23}}(-1)^{j_{23}+j_{31}+j_{12}}(2j_{23}+1)\begin{Bmatrix}j_1 & j_2 & j_{12}\\ j_3 & j & j_{23}\end{Bmatrix}\begin{Bmatrix}j_2 & j_3 & j_{23}\\ j_1 & j & j_{12}\end{Bmatrix}=\begin{Bmatrix}j_3 & j_1 & j_{31}\\ j_2 & j & j_{12}\end{Bmatrix} \qquad (23)$$

and

$$\begin{aligned}\sum_{j_{124}}(-1)^{j_1+j_2+j_3+j_4+j_{12}+j_{23}+j_{14}+j_{123}+j_{124}}(2j_{124}+1)&\begin{Bmatrix}j_3 & j_2 & j_{23}\\ j_{14} & j & j_{124}\end{Bmatrix}\begin{Bmatrix}j_2 & j_1 & j_{12}\\ j_4 & j_{124} & j_{14}\end{Bmatrix}\begin{Bmatrix}j_3 & j_{12} & j_{123}\\ j_4 & j & j_{124}\end{Bmatrix}\\
&=\begin{Bmatrix}j_1 & j_2 & j_{12}\\ j_3 & j_{123} & j_{23}\end{Bmatrix}\begin{Bmatrix}j_{23} & j_1 & j_{123}\\ j_4 & j & j_{14}\end{Bmatrix}. \qquad (24)\end{aligned}$$

In particular, for the first term of (22), the sum over J_2 can be carried out by (19), and then the sum over J_1 can be done again by (19); the second term is treated in a similar manner. For the third term, we first apply (24) and then (23). For the fourth term, we sum over J_2 by (19), and then the sum over J_1 can be shown to vanish by a construction similar to expression (18). In a similar manner, the fifth term also vanishes. Thus it can be seen that the interference term between the isotropic polarization potential and the quadrupole potential always vanishes. Thus Eq. (22) becomes

$$\sigma_d(j)_{l\geq 1} = \frac{4\pi}{25}\,\frac{(2j+1)}{5}\,(j0j0|20)^2 \sum_{l=1} \left[\frac{Q^2}{l(2l-1)(2l+3)} + \frac{2\pi\alpha_2 Qk(l+1)}{(2l-1)^2(2l+1)(2l+3)^2} + \frac{Q^2}{(l+2)(2l+1)(2l+5)} \right.$$

$$+ \frac{2\pi\alpha_2 Qk(l+1)}{(2l+1)^2(2l+3)(2l+5)^2} - \frac{4l(l+1)^2(l+2)}{[(2l+1)(2l+2)(2l+3)][(2l-1)(2l)(2l+4)(2l+5)]^{1/2}}$$

$$\left. \times \begin{Bmatrix} 2 & l+1 & l+1 \\ 1 & l & l \end{Bmatrix} \frac{Q^2}{l(l+1)^2(l+2)} + \frac{\pi\alpha_2 Qk}{(l+1)(2l+2)(2l+3)} \left(\frac{1}{l(2l+5)} + \frac{1}{(l+2)(2l-1)} \right) \right]. \tag{25}$$

Simplifying further, Eq. (25) becomes

$$\sigma_d(j)_{l\geq 1} = \frac{4\pi j(j+1)}{5(2j-1)(2j+3)} \left[Q^2 \sum_{l=1} \left(\frac{1}{l(2l-1)(2l+3)} - \frac{2}{(l+1)(2l+1)(2l+3)} + \frac{1}{(l+2)(2l+1)(2l+5)} \right) \right.$$

$$\left. + 2\pi\alpha_2 Qk \left(\frac{l+1}{(2l-1)^2(2l+1)(2l+3)^2} + \frac{l+1}{(2l+1)^2(2l+3)(2l+5)} - \frac{2(2l^2+4l-1)}{(2l-1)(2l+1)^2(2l+3)^2(2l+5)} \right) \right]. \tag{26}$$

As the whole contribution is very small, we will drop the second term in large parentheses, i.e., the linear term in k. Applying the method of partial fraction, the sum in the first large parentheses becomes

$$\sum_{l=1} \left(-\frac{1/3}{l} + \frac{1/2}{2l-1} + \frac{1/6}{2l+3} + \frac{2}{l+1} - \frac{2}{2l+1} - \frac{2}{2l+3} - \frac{1/3}{l+2} + \frac{1/6}{2l+1} + \frac{1/2}{2l+5} \right). \tag{27}$$

These terms may be rearranged to form alternating harmonic series (which sum to ln2), i.e.,

$$\frac{1}{2}\sum_{l=1}\left(\frac{1}{2l-1} - \frac{1}{2l}\right) + \frac{1}{6}\sum_{l=1}\left(-\frac{1}{2l} + \frac{1}{2l+1}\right) - 2\sum_{l=1}\left(\frac{1}{2l+1} - \frac{1}{2l+2}\right) - 2\sum_{l=1}\left(-\frac{1}{2l+2} + \frac{1}{2l+3}\right)$$

$$+ \frac{1}{6}\sum_{l=1}\left(\frac{1}{2l+3} - \frac{1}{2l+4}\right) + \frac{1}{2}\sum_{l=1}\left(-\frac{1}{2l+4} + \frac{1}{2l+5}\right). \tag{28}$$

Completing the series by adding (and subtracting) terms as required, we obtain

$$\tfrac{1}{2}\ln 2 + \tfrac{1}{6}(\ln 2 - 1) - 2(\ln 2 - 1 + \tfrac{1}{2}) - 2(\ln 2 - 1 + \tfrac{1}{2} - \tfrac{1}{3})$$

$$+ \tfrac{1}{6}(\ln 2 - 1 + \tfrac{1}{2} - \tfrac{1}{3} + \tfrac{1}{4}) + \tfrac{1}{2}(\ln 2 - 1 + \tfrac{1}{2} - \tfrac{1}{3} + \tfrac{1}{4} - \tfrac{1}{5}). \tag{29}$$

Finally we have

$$\sigma_d(j)_{l\geq 1} = \frac{4\pi Q^2 j(j+1)}{5(2j-1)(2j+3)}\left(2 - \tfrac{8}{3}\ln 2 + \tfrac{1}{90}\right)$$

$$= \frac{4\pi Q^2 j(j+1)}{5(2j-1)(2j+3)}(0.16). \tag{30}$$

It is interesting to note that about 75% of the contribution to Eq. (30) comes from the term $l = 1$ (p and d waves). Comparing Eq. (30) with Eq. (20), we find that higher partial waves contribute only a further correction of $0.16/0.75 \simeq 20\%$ to $\sigma_d(j)_{l=0}$.

C. Nondiagonal T matrices

To evaluate the nondiagonal contributions, we must return to Eq. (3). Note that the nondiagonal T matrices are given by[11]

$$T^{Jj}_{l'l} = 2ie^{i(\eta^J_{jl} + \eta^J_{jl'})}\beta^{Jj}_{l'l},$$

where

$$\beta^{Jj}_{l'l} = -2k(jl', J|P_2|jl, J)\int_0^\infty j_{l'}(kr)j_l(kr)(Q/r^3)r^2\,dr. \tag{31}$$

The angular factor is a slight generalization of Eq. (12), i.e.,

$$(jl'J|P_2|jl, J) = \frac{(-1)^J}{5}(2j+1)[(2l'+1)(2l+1)]^{1/2}$$

$$\times (l'0l0|20)(j0j0|20)\begin{Bmatrix} j & l & J \\ l' & j & 2 \end{Bmatrix}. \tag{32}$$

The radial integral containing Bessel functions J can be evaluated analytically:

$$-2kQ\int_0^\infty J_{l'+1/2}(r)J_{l+1/2}(r)\frac{dr}{r^2}=-Qk\frac{4(-1)^{1/2(l'-l)}}{(1-l+l')(1+l-l')(l+l'+2)(l+l')}$$

$$=\frac{4Qk}{3(l+l'+2)(l+l')}\,, \tag{33}$$

since $l'=l\pm2$ is the only case of interest. Now in Eq. (3) we note that

$$T^{J_1j^*}_{l_1'l_1}T^{J_2j}_{l_2'l_2}+(\text{c.c.})=4\beta^{J_1j}_{l_1'l_1}\,\beta^{J_2j}_{l_2'l_2}\,[2\cos(\eta^{J_1}_{jl_1'}+\eta^{J_1}_{jl_1}-\eta^{J_2}_{jl_2'}-\eta^{J_2}_{jl_2})]\simeq4\times2\beta^{J_1j}_{l_1'l_1}\,\beta^{J_2j}_{l_2'l_2}\,, \tag{34}$$

since we consistently neglect terms of order k^2 in comparison with 1. With this point in mind, we may write the pure nondiagonal contributions to Eq. (3) as

$$\sigma_d(j)_{\text{nondiag}}=\frac{4\pi}{k^2(2j+1)}\sum_{l'lJ}(2J+1)\;\beta^{Jj^2}_{l'l}+\frac{1}{3}\sum_{J_1J_2l_1l_1'l_2l_2'}2\beta^{J_1j}_{l_1'l_1}\,\beta^{J_2j}_{l_2'l_2}$$

$$\times(-1)^{1/2(-l_1+l_2-l_1'+l_2')}[(2l_1+1)(2l_1'+1)(2l_2+1)(2l_2'+1)]^{1/2}(2J_1+1)(2J_2+1)$$

$$\times(l_10l_2|10)(l_1'0l_2'0|10)\begin{Bmatrix}l_2&l_1&1\\J_1&J_2&j\end{Bmatrix}\begin{Bmatrix}l_2'&l_1'&1\\J_1&J_2&j\end{Bmatrix}. \tag{35}$$

Substituting β for Eqs. (31)–(33), and applying sum rules [Eqs. (19), (23), and (24)], we obtain

$$\sigma_d(j)_{\text{nondiag}}=4\pi\Bigg(\sum_{ll'}(2j+1)(2l+1)(2l'+1)(l'0l0|20)^2(j0j0|20)^2\frac{(-1)^{l-l'}16Q^2}{5^3\,3^2(l+l')^2(l+l'+2)^2}$$

$$+\frac{1}{3}\sum_{l_1l_1'l_2l_2'}2(2j+1)(2l_1+1)(2_l'+1)(2l_2+1)(2l_2'+1)(l_10l_20|10)(l_1'0l_2'0|10)$$

$$\times(l_10l_1'0|20)(l_20l_2'0|20)(j0j0|20)^2\frac{16Q^2}{5^3\,3^2(l_1+l_1')(l_2+l_2')(l_1+l_1'+2)(l_2+l_2'+2)}\Bigg). \tag{36}$$

Because of the restrictions imposed by the $3j$ symbol, all summations reduce to a single sum as follows:

$$\sigma_d(j)_{\text{nondiag}}=4\pi\frac{Q^2j(j+1)}{(2j-1)(2j+3)}\left(\frac{2}{15}\sum_{l=1}\frac{1}{(2l+2)(2l+3)(2l+4)}+\frac{8}{15}\sum_{l=1}\frac{1}{(2l+3)(2l+4)(2l+5)}\right). \tag{37}$$

As before, we obtain by partial fractions

$$\sigma_d(j)_{\text{nondiag}}=\frac{4\pi Q^2j(j+1)}{15(2j-1)(2j+3)}\left[\sum_{l=1}\left(\frac{1}{2l+2}-\frac{2}{2l+3}+\frac{1}{2l+4}\right)+4\sum_{l=1}\left(\frac{1}{2l+3}-\frac{2}{2l+4}+\frac{1}{2l+5}\right)\right], \tag{38}$$

and by the alternating harmonic series

$$\sigma_d(j)_{\text{nondiag}}=\frac{4\pi Q^2j(j+1)}{15(2j-1)(2j+3)}\left(\tfrac{3}{2}-2\ln2+8\ln2-\tfrac{16}{3}\right). \tag{39}$$

D. Nondiagonal T matrices, cross term

Finally, we consider the cross term between diagonal and nondiagonal T matrices. In Eq. (3) the first term contains no cross terms; the second contributes

$$\sigma_d(j)_{\text{cross}}=\frac{4\pi}{3k^2(2j+1)}\sum_{J_1J_2l_1l_2l_2'}2\sin\eta^{J_1}_{jl_1}\,\beta^{J_2j}_{l_2'l_2}\,(-1)^{(l_2'+l_2)/2-l_1}[(2l_2+1)(2l_2'+1)]^{1/2}$$

$$\times(2l_1+1)(2J_1+1)(2J_2+1)(l_10l_20|10)(l_10l_2'0|10)\begin{Bmatrix}l_2&l_1&1\\J_1&J_2&j\end{Bmatrix}\begin{Bmatrix}l_2'&l_1&1\\J_1&J_2&j\end{Bmatrix}, \tag{40}$$

where we have used the same approximations as in Sec. III C. Substituting for η and β, we can again apply sum rule (24) and then (23), simplifying Eq. (40) to

$$\sigma_d(j)_{\text{cross}} = 4\pi \sum_{l_1 l_2 l_2'} 2(2j+1)(2l_1+1)^2(2l_2+1)(2l_2'+1)(l_1 0 l_2 0|10)(l_1' 0 l_2 0|10)(l_1 0 l_1 0|20)$$

$$\times (l_2 0 l_2' 0|20)(j0j0|20)^2 \frac{(-1)^{l_1 - l_2'} 16 Q^2}{(l_2+l_2')(l_2+l_2'+2)\, 3^2\, 5^3 (2l_1)(2l_1+2)} \begin{Bmatrix} l_1 & l_1 & 2 \\ l_2' & l_2 & 1 \end{Bmatrix}. \tag{41}$$

As before, this becomes

$$\sigma_d(j)_{\text{cross}} = 4\pi \frac{Q^2 j(j+1)}{(2j-1)(2j+3)} \frac{8}{15} \sum_{l=1} \frac{1}{(2l+1)(2l+2)(2l+3)(2l+4)(2l+5)} . \tag{42}$$

Again by partial fractions, Eq. (42) can be written as

$$\sigma_d(j)_{\text{cross}} = \frac{4\pi Q^2 j(j+1)}{15(2j-1)(2j+3)} \sum_{l=1} \left(\frac{1/3}{2l+1} - \frac{4/3}{2l+2} + \frac{2}{2l+3} - \frac{4/3}{2l+4} + \frac{1/3}{2l+5} \right), \tag{43}$$

which sums to

$$\sigma_d(j)_{\text{cross}} = \frac{4\pi Q^2 j(j+1)}{15(2j-1)(2j+3)} \left(\frac{8}{3} \ln 2 - \frac{16}{9} \right).$$

E. Final results, $\sigma_d(j)$

To obtain the general diffusion cross section, we collect these partial results and sum them up. Adding up Eqs. (10), (20), (30), (39), and (44), we obtain

$$\sigma_d(j) = 4\pi A^2 \left[1 + \frac{Q^2}{A^2} \left(\frac{j(j+1)}{(2j-1)(2j+3)} \right) \left(\frac{481}{2700} + \frac{2}{45} \ln 2 \right) + \left[\frac{4\pi \alpha_0}{5A} + \frac{\pi \alpha_2 Q}{25 A^2} \left(\frac{j(j+1)}{(2j-1)(2j+3)} \right) \right] k + \cdots \right] . \tag{45}$$

Note that Eq. (45) is completely general. For the ground state $j=0$, we recover Eq. (10). For other values of j, the new term is only mildly dependent on j, since the first term in large parentheses only varies from 0.4 for $j=1$ to 0.25 as $j \to \infty$. In any case, this term is usually small, stemming from the small value of the second term in large parentheses, 0.21. Specifically, for H_2 in the $j=1$ state, this term has a value of 0.012. This means that at zero energy the diffusion cross section is larger by 1.2% for orthohydrogen than for parahydrogen. At other energies, the above statement is essentially also true, since the change in the coefficient of the linear term in k (though incompletely calculated) is only ≈0.2%.

In experiment ii on normal hydrogen, which is composed of 25% of the molecules in the $j=0$ and 75% in the $j=1$ state, Gibson[7] found that, to within the error limits (±5%), the diffusion cross sections for these respective states are equal. Calculations based on the close-coupling approximation indicate that they are about equal.[9] Our present work shows that the latter is roughly 1% larger than the former, which was shown in Fig. 1, and has the same shape. This slight difference is not siginificant enough to cast doubt on the analysis of the swarm data in experiment ii.

IV. RESULTS FOR D_2, N_2, AND O_2

For molecules heavier than H_2, it is usually impractical to perform the experiment at a low enough temperature that substantially all molecules are in one or even two rotational states. In these cases, the measured diffusion cross section represents a value averaged over all rotational states weighted by their population number at the experimental temperature. Results for each of the cases D_2, N_2, and O_2 are discussed separately below.

A. Results for D_2

The experimental data on D_2 at 77 °K were analyzed by Gibson,[7] who gave the population distribution as 56.6% in the $j=0$, 33.0% in the $j=1$, 10.1% in the $j=2$, and 0.3% in the $j=3$, state. No experimental values of the diffusion cross sections were given, since the various diffusion cross sections could no longer be uniquely determined. Nevertheless, in analyzing the power-loss data it was again assumed that the diffusion cross sections for each value of j were all equal, and that this cross section for D_2 had to be smaller than the one for H_2 in order to get good fits for the rotation-excitation cross sections. Since the quadrupole moment[18] of D_2 differs from that of H_2 by only 2%, the assumption made by Gibson is quite valid, as for the case of H_2. The polarizability α_0 of D_2 is about 1.2% lower[13] than the one for H_2. So this fact is consistent with a lower σ_d for D_2, provided that the scattering length for D_2 is not larger. Without further experimental data, we are unable to shed light on the scattering length of D_2.

In Gibson's analysis, the diffusion cross section for D_2 was found to fall below that of H_2 at the rate of 3% per eV starting with the same value at zero energy. Theoretically this difference is expected to be proportional to k rather than k^2. In any case it is less than 1% in the energy range of interest, and the diffusion cross section for D_2 and H_2 may be taken as the same.

B. Results for N_2

Experimental results for the diffusion cross section in N_2 are available from the work of Engelhardt, Phelps, and Risk.[19] The experiment was conducted at 77°K, while the rotational constant of N_2 is only 0.24 meV, corresponding to a rotational temperature of 2.9°K. Therefore the measured values of the cross section represent an average over a good number of rotational states. Specifically, the measured diffusion cross section is given by

$$\bar{\sigma}_d = \frac{\sum_j \sigma_d(j)\rho_j(2j+1)e^{-0.038j(j+1)}}{\sum_j \rho_j(2j+1)e^{-0.038j(j+1)}}, \tag{46}$$

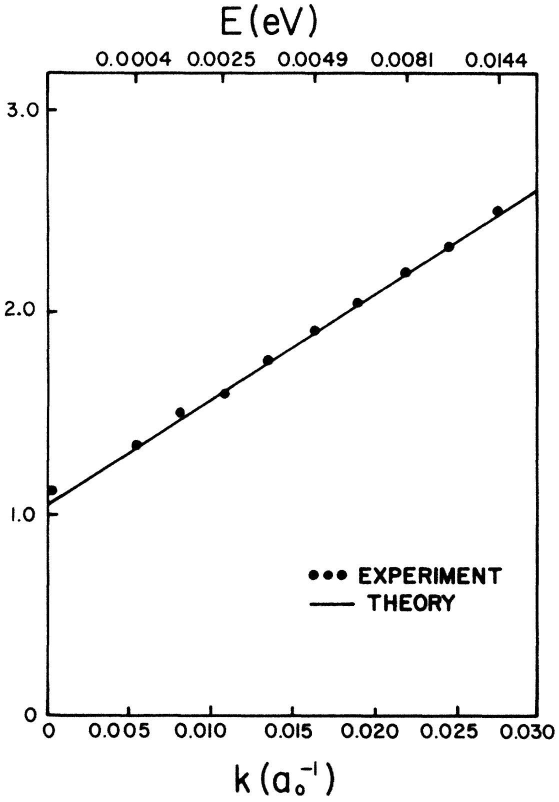

FIG. 2. Diffusion cross section in N_2 at 77 °K, as a function of the wave vector k (bottom scale) and as a function of the energy E (top scale).

where ρ_j is a statistical weight arising from nuclear-spin considerations and has the value 2 when j is even, 1 when j is odd.

Figure 2 shows the experimental values of $\bar{\sigma}_d$ plotted against the wave vector k. Again, as in Fig. 1, we find that a straight line fits very well. If we make a naive assumption that the effect of averaging over a large number of rotational states is equivalent to averaging over all orientations of the molecule and use the j-independent Eq. (10), we obtain $A = 0.52$ and $\alpha_0 = 9.8$. The experimental values[20] for the polarizabilities of N_2 are $\alpha_0 = 11.9$ and $\alpha_2 = 4.2$. Therefore we see that the above assumption is far from satisfactory. Now let us turn to Eq. (45), which properly accounts for the dependence of σ_d on the rotational state j. Substituting into Eq. (46), we obtain

$$\bar{\sigma}_d = 4\pi A^2 + [(4\pi)^2/5]\,\alpha_0 Ak + 4\pi \times (0.21)Q^2\bar{f} + (4\pi^2/25)\alpha_2 Qk\bar{f}, \tag{47}$$

where

$$\bar{f} = \frac{\sum_j [j(j+1)/(2j-1)(2j+3)]\rho_j(2j+1)e^{-0.038j(j+1)}}{\sum_j \rho_j(2j+1)e^{-0.038j(j+1)}}. \tag{48}$$

From the discussion at the end of Sec. II, we can easily surmise that $\bar{f}$ should be between 0.25 and 0.40, and if the molecule's rotational temperature is much less than the actual temperature, $\bar{f}$ should have a value $\gtrsim 0.25$. Actual evaluation of Eq. (48) yields $\bar{f} = 0.30$. In Eq. (47) we have one unknown A and three parameters α_0, α_2, and Q known from other experiments. For N_2 both α_0 and α_2 are accurately known and have already been given. Q is less accurately known; we will use the recommended value of Stogryn and Stogryn,[18] which is $-1.13ea_0^2$. Clearly, to fit Eq. (47) to the straight line in Fig. 2, we cannot assume all four parameters to be unknown. Instead, we can only determine A and perform a consistency test on the other three parameters. Our procedure is to use at $k = 0$ the known value of Q to determine A, which turns out to be $0.44a_0$. This value in turn can now be used to evaluate α_0, assuming the value of α_2 to be correct. It should be recognized, however, that the accuracy of α_2 is of no concern, since the term involving α_2 is only of the order of 1% of the one involving α_0. The value of α_0 so obtained is $11.6a_0^3$, which compares quite favorably with the experimental value of $11.9a_0^3$.

The excellent agreement between theory and experiment in Fig. 2 at all energies including zero can be attributed, in part, to the careful analysis of the experimental data.[19] In particular, the superelastic cross sections were explicitly included in deducing the diffusion cross section from the raw data. These cross sections are much more important in N_2 than in H_2 because of the much lower rotational temperature and the larger quadrupole moment.

C. Results for O_2

The experimental results for O_2 conducted at room temperature by Hake and Phelps[21] are shown in Fig. 3. Unlike the results for H_2 and N_2, it is not at all clear that the experimental points here fall on a straight line, even if we ignore the point at $k = 0$. Fortunately, it is easy to understand why MERT may not apply to low-energy e-O_2 scattering at all, since the joint system forms a bound state O_2^-. If the electron is captured into the bound state, it will interact repeatedly with the potential $V(\vec{r})$, so that the Born which is a first-order approximation is no longer valid. Furthermore, being captured will enable the electron to sample the unknown short-range potential in spite of its long wavelength. Therefore it is not at all surprising that MERT as developed in this paper may not apply to e-O_2 scattering at all. Nevertheless, it is of interest to ask whether the data could be empirically fitted to MERT in a meaningful way. We proceed to attempt such a fit.

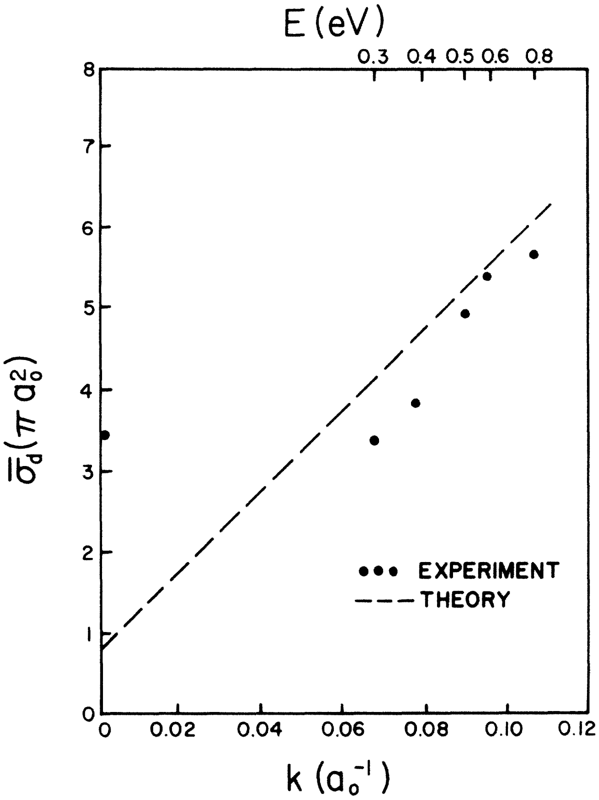

FIG. 3. Diffusion cross section in O_2 at 300 °K, as a function of the wave vector k (bottom scale) and as a function of the energy E (top scale).

From Stogryn and Stogryn,[18] we obtain $Q = -0.29ea_0^2$ for O_2, and from Hirschfelder *et al.*[20] we have $\alpha_0 = 10.8$ and $\alpha_2 = 5.1a_0^3$. Note that in Eq. (47) only the squares of A and Q contribute at $k = 0$, and therefore they both have to be small in magnitude in order to fit the data in Fig. 3. As we have seen, $|Q|$ is indeed small; A has to be determined by a fitting procedure. We will ignore the point at $k = 0$ as before, since its precision is marred by superelastic processes. Hence A has to be evaluated from the intercept of the fitted straight line; however, we can see from Fig. 3 that the large scatter in the data will not yield a meaningful value of A. Instead we will try to determine A from the slope of the graph using the known values of the polarizabilities. Using a value of 50 for the slope, we obtain $A = 0.46a_0$. Substituting this and all other values of the parameters into Eq. (47), we obtain the dotted line in Fig. 3. Clearly, the fit so obtained is hardly satisfactory; however, one cannot completely rule out MERT empirically, since it is not inconceivable that the experimental points can have errors of 20%.[22]

Actually, the cross section for e-O_2 scattering should be the incoherent sum of doublet and quartet partial cross sections in the ratio of 1:2. Our MERT analysis should apply to quartet scattering, but not to doublet scattering, owing to the bound state $^2\Pi_g$. It is desirable to have a theory which takes the bound state into consideration before meaningful comparisons can be made with experiment.

V. CONCLUSION

In this paper we have extended the modified effective-range theory to electron-molecule scattering—in particular, to homonuclear diatomic molecules. The correction to the original MERT for atoms arises in the lowest-order (constant) term and is proportional to $(Q/A)^2$, where Q is the quadrupole moment and A is the scattering length, and in addition is *dependent* on the rotational state j. For parahydrogen ($j = 0$), this correction is zero, and the experimental diffusion cross section agrees with MERT very well. For orthohydrogen, this correction term is of the order of 1%, owing to the smallness of (Q/A), and is therefore insignificant. All evidence, theoretical and experimental,[23] shows that the diffusion cross sections in D_2 and in H_2 differ by less than 1%. In the case of N_2, Q is a factor of 2 larger and A a factor of 2 smaller than for H_2, and hence the correction is a factor of 16 larger than for H_2. Therefore this correction term is essential in obtaining

agreement between MERT and experiment. In O_2, the existence of a bound state, so far ignored in the theory, renders comparison between theory and experiment inconclusive.
parison between theory and experiment meaningless.

Although this work so far leaves little doubt as to the correctness of this new term proportional to $(Q/A)^2$, it is interesting to seek circumstances where this term might become the dominant term in the expression for the diffusion cross section. First, there exist homonuclear diatomics with large quadrupole moments; e.g.,[18] $10.2ea_0^2$ for Li_2 and $4.5ea_0^2$ for Cl_2. Second, in a sequence of gases with similar electronic structure, the scattering length often changes in a systematic and predictable manner. For example, in the rare gases, A decreases as the atomic number increases, changing sign between neon and argon. Therefore it is often possible to predict which molecules will have a small $|A|$. Experiments in gases with large $|Q/A|$ should be encouraged to further confirm this theory.

Finally, as most molecules do have a dipole moment, further theoretical work is necessary to extend the present work to include those cases.

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